

19



Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

0 145 471
A2

12

EUROPEAN PATENT APPLICATION

21 Application number: 84308541.6

51 Int. Cl.: C 22 C 38/26

22 Date of filing: 07.12.84

30 Priority: 12.12.83 US 560129

71 Applicant: Armco Inc., 703 Curtis Street, Middletown Ohio 45043 (US)

43 Date of publication of application: 19.06.85
Bulletin 85/25

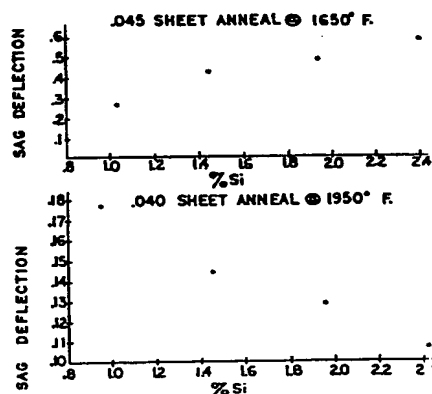
72 Inventor: Gorman, Mark D., 321 Gallisher Road, Lebanon Ohio (US)

64 Designated Contracting States: BE DE FR GB IT SE

74 Representative: Grundy, Derek George Ritchie et al, CARPMAELS & RANSFORD 43, Bloomsbury Square, London WC1A 2RA (GB)

54 High temperature ferritic steel.

57 An alloy steel having good formability, cyclic oxidation resistance and creep strength at elevated temperatures above 1000°F and particularly above about 1500°F (816°C) after a final anneal at 1850° to 2050°F (1010° to 1120°C), comprising 0.05% maximum carbon, about 2% maximum manganese, 1.0% to 2.0% silicon, 6% to 25% chromium, up to about 5% molybdenum, with the sum of chromium and molybdenum being at least 8.0%, 0.05% maximum nitrogen, at least one of titanium, zirconium, tantalum and columbium in an amount equal to the stoichiometric equivalent of the carbon plus nitrogen contents, and containing at least 0.1% uncombined columbium, less than 0.5% aluminum and balance essentially iron.



EP 0 145 471 A2

HIGH TEMPERATURE FERRITIC STEEL

1

This invention relates to a ferritic steel having improved cyclic oxidation resistance and creep strength at elevated temperature. More particularly, in the form of cold rolled strip, sheet, bar, rod and wire which has been subjected to a final anneal at 1850° to 2050°F (1010° to 1120°C), a preferred steel of the invention having a ferritic microstructure exhibits the above properties by reason of purposeful addition of silicon, a carbide and nitride former, and columbium within critical limits. Control of aluminum to a low value confers excellent weldability and formability without sacrifice of other properties. A synergistic improvement in creep strength and improved cyclic oxidation resistance at elevated temperature results from the combination of a silicon addition within the broad range of 0.8% to 2.25%, addition of sufficient carbide and nitride former to combine with substantially all the carbon and the nitrogen, addition of a small amount of columbium substantially all of which will be uncombined as a result of the carbide and nitride former addition, and a final high temperature anneal. The combination of properties is achieved throughout a wide range of chromium levels, viz. from about 1% to about 25%, but a fully ferritic microstructure may not be obtained at chromium plus molybdenum levels less than about 8%.

The automotive industry is a large user of flat rolled ferritic stainless steels for engine exhaust components. A standard stainless steel for this purpose has a nominal composition of about 0.03% maximum carbon, about 0.25% manganese, residual phosphorus and sulfur, about 0.5% silicon, about 12% chromium, about 0.2% nickel, about 0.4% titanium, about 0.1% maximum aluminum, about 0.02% maximum nitrogen, and balance essentially iron.

35

1 The present invention provides a substitute for the
above stainless steel, having improved properties, not
only for automotive exhaust components, but also for
powder metal articles and welded articles.

5 A steel having substantially improved elevated
temperature strength and oxidation resistance, in compari-
son to the above standard steel, is disclosed in United
States Patent 4,261,739. In broad ranges the steel of
this patent consists essentially of, in weight percent,
10 from about 0.01% to 0.06% carbon, about 1% maximum manga-
nese, about 2% maximum silicon, about 1% to about 20%
chromium, about 0.5% maximum nickel, about 0.5% to about
2% aluminum, about 0.01% to 0.05% nitrogen, 1.0% maximum
titanium, with a minimum titanium content of 4 times the
15 percent carbon plus 3.5 times the percent nitrogen, about
0.1% to 1.0% columbium, with the sum total of titanium
plus columbium not exceeding about 1.2%, and remainder
essentially iron. A preferred steel in accordance with
this patent has a nominal composition of about 0.02%
20 carbon, about 0.25% manganese, about 0.02% phosphorus,
about 0.005% sulfur, about 0.5% silicon, about 12.0%
chromium, about 0.20% nickel, about 0.02% nitrogen, about
0.3% titanium, about 0.6% columbium, about 1.2% aluminum,
and balance essentially iron. Such a preferred steel
25 exhibits optimum elevated temperature strength and
oxidation resistance in the cold rolled form when it is
subjected to a final anneal at 1850° to 2050°F.

While this patent recognizes that aluminum in excess
of about 1% can affect weldability adversely, relatively
30 high aluminum levels, with a minimum of about 0.75%, must
nevertheless be present in order to obtain the excellent
elevated temperature oxidation resistance of this steel.
Accordingly, the likelihood of poor weldability under
some types of welding operations is present in the steel
35 of this patent.

1 The present invention constitutes a discovery that
silicon can be substituted at least partially for alumi-
num and also partially for chromium, with a consequent
improvement in weldability while at the same time retain-
5 ing excellent oxidation resistance and creep strength at
elevated temperature.

 An article entitled "Influence of Columbium on the
870°C Creep Properties of 18% Chromium Ferritic Stainless
Steels" by J. N. Johnson, SAE Technical Paper Series,
10 810035, February 1981, reports tests on an 18% chromium
steel containing molybdenum, titanium and columbium. In
the test samples, silicon ranged from 0.08% to 0.74%, and
uncombined columbium ranged from 0.11% to 0.58%. It was
concluded on the basis of reported tests that a
15 significant improvement in 870°C creep strength of 18%
chromium steels was obtained with the combination of
about 0.5% free (uncombined) columbium and a high final
annealing temperature at 925° to 1150°C (about 1700° to
about 2100°F). In these test samples, aluminum was
20 absent except in one sample which contained 1.89%
aluminum, 0.71% silicon, 0.35% titanium and no columbium.
This article contains no discussion regarding the effect
of silicon or aluminum, other than reference to a Laves
phase which, although primarily intermetallic compounds
25 of iron-molybdenum or iron-columbium, may contain
substitutional elements such as chromium, manganese and
silicon.

 "Effect of Molybdenum on Creep Properties of a
Ferritic 18Cr-Nb-Ti Steel for Catalytic Converters", J.
30 D. Redmond et al, Journal of Metals, February 19, 1981,
pages 19 - 25 reports the effect of molybdenum and
columbium on creep-rupture properties of an 18% chromium
steel. It is concluded that an additional strengthening
mechanism in molybdenum-containing steels may result from
35 the change in composition of the Laves phase where

1 columbium decreases with increasing molybdenum contents.
The displaced columbium is then available for further
dispersion strengthening by carbide precipitation.

Ferritic, chromium-containing steels containing one
5 or more of aluminum, titanium, columbium, silicon or
zirconium are disclosed in United States Patents
3,909,250; 3,782,925 and 3,759,705, and British Patent
1,262,588. These alloys, while exhibiting improved
oxidation resistance at elevated temperature,
10 nevertheless have poor creep strength at elevated
temperature and possible weldability problems.

NASA TN-D 7966 published in 1975, discloses
modifications in 15% and 18% chromium ferritic steels
wherein it was concluded that addition of 0.45% to 1.25%
15 tantalum to a nominal 18% chromium, 2% aluminum, 1%
silicon and 0.5% titanium steel provided the greatest
improvement in fabricability, tensile strength and
stress-to-rupture strength at 1800°F, along with
oxidation resistance and corrosion resistance at elevated
20 temperature. After cold rolling to final thickness, a
final anneal at 1000°C was conducted in the processing of
these test alloys.

An article by H. E. Evans et al, in Oxidation of
Metals, Vol. 19, Nos. 1/2, 1983, pages 1 - 18, describes
25 the influence of silicon on the oxidation resistance of
nitrided austenitic stainless steels of nominal 2%
chromium - 25% nickel composition. A series of such
steels, also containing from 0.005% to 0.050% carbon,
0.42% to 0.74% manganese, 1.44% to 1.56% titanium, and
30 0.05% to 0.21% columbium, was prepared with silicon
levels ranging from 0.05% to 2.35%. cold rolled strips
were nitrided at 1423°K (2102°F) and tested for oxidation
resistance at 1123°K (1562°F). It was found that
chromium-rich oxide surface films developed in all cases,
35 and the film thickness increased parabolically with time.

1 The parabolic rate constant was at a minimum at 0.92%
silicon. The reason for failure of higher silicon levels
(about 1.5% to 2.35%) to improve oxidation resistance was
5 postulated as being perhaps due to removal of silicon
from solution by precipitation.

The present invention constitutes a discovery that
improvement in weldability can be combined with excellent
cyclic oxidation resistance and creep strength at ele-
vated temperature above 1000°F (538°C) and particularly
10 above 1500°F (816°C) in a ferritic steel. This is
achieved in a preferred ferritic steel by substitution of
silicon for at least part of the aluminum required in
prior art steels having high oxidation resistance, by
providing a relatively small content of uncombined colum-
15 bium with reliance on titanium, zirconium, tantalum
and/or columbium to combine with carbon and nitrogen, and
by subjecting the ferritic steel to a final anneal at
1850° to 2050°F (1010°C to 1120°C). While the cyclic
oxidation resistance at elevated temperature of the steel
20 of the present invention is slightly inferior to that of
the previously mentioned United States Patent 4,261,739,
creep strength of the present steel is slightly superior
to that of said patent, and cyclic oxidation resistance
and creep strength are substantially superior to that of
25 the above-mentioned standard steel used for engine
exhaust components which is commonly designated as Type
409.

It is an object of the present invention to provide
a substantially ferritic steel at all temperatures having
30 a wide chromium range which exhibits the combination of
excellent oxidation resistance and strength at elevated
temperature together with excellent weldability and which
at the same time contains a minimum of expensive alloying
ingredients.

35 According to the broadest aspect of the invention

1 there is provided an alloy steel exhibiting good
formability and improved cyclic oxidation resistance and
creep strength at elevated temperatures above 1000°F
(538°C) after a final anneal at 1850° to 2050°F (1010° to
5 1120°C), consisting essentially of, in weight percent,
0.05% maximum carbon, about 2% maximum manganese, 1.0% to
2.0% silicon, 6% to 25% chromium, up to about 5%
molybdenum, with the sum of chromium and molybdenum being
at least 8%, 0.05% maximum nitrogen, at least one of
10 titanium, zirconium, tantalum, and columbium, said
titanium, zirconium, tantalum and columbium being present
in an amount at least equal to the stoichiometric
equivalent of the percent carbon plus the percent
nitrogen, and containing at least 0.1% uncombined
15 columbium, less than 0.5% aluminum, and balance
essentially iron.

A preferred ferritic steel within the above broad
ranges which combines the further desirable properties of
weldability and formability, consists essentially of, in
20 weight percent, about 0.03% maximum carbon, about 1%
maximum manganese, 1.0% to 2.0% silicon, 8% to 20%
chromium, about 0.5% maximum molybdenum, about 0.03%
maximum nitrogen, about 0.5% maximum titanium with a
minimum titanium content of 4 times the percent carbon
25 plus 3.5 times the percent nitrogen, about 0.3% maximum
columbium with at least 0.10% uncombined columbium, less
than 0.5% aluminum, and balance essentially iron.
Uncombined columbium will be understood to mean that
which is not combined with carbon and/or nitrogen.

30 Reference is made to the accompanying drawing which
is a graphic comparison of sag resistance as a function
of silicon content at two different final annealing
temperatures.

As disclosed in the above-mentioned United States
35

1 Patent 4,261,739, conventional final annealing tempera-
tures for ferritic steels range from about 1400° to about
1700°F (760° to 925°C). As was the case in that patent,
5 it has been found that a higher final anneal within the
range of 1850° to 2050°F (1010° to 1120°C) contributes
significantly to improved elevated temperature creep
strength in the steel of the present invention.
Improvement in high temperature creep strength may be
attributed to an increase in the final grain sizes, solid
10 solution strengthening of the ferritic matrix, and the
presence of carbide and nitride precipitates of titanium,
zirconium, tantalum, and/or columbium which pin the grain
boundaries, thus retarding the creep mechanism. A
columbium-silicon rich Laves phase which improves creep
15 strength, apparently develops at a lower columbium level
than obtained in United States Patent 4,261,739 due to
synergism with silicon.

Surprisingly, cyclic oxidation resistance is also
dramatically improved due to the higher silicon level
20 either with or without a higher final anneal and either
with or without a columbium addition.

A broad maximum of 0.05% carbon and 0.05% nitrogen
must be observed in order to maintain a fully ferritic
structure and to minimize the amounts of the carbide and
25 nitride forming element or elements needed to stabilize
the steel. Preferably carbon and nitrogen are each
restricted to a maximum of about 0.03%.

Manganese could be present for its strengthening
effect, but a broad maximum of about 2%, and a preferred
30 maximum of 1%, should be observed, since it does not form
ferrite and may adversely affect the oxidation resistance
of ferritic steels.

Phosphorus and sulfur may be present in the usual
residual amounts without adverse effect.

35 Chromium may range between about 1% and 25% in order

1 to obtain a desired level of corrosion and oxidation
resistance at minimum cost, for a particular application.
A preferred range of about 8% to about 20% chromium con-
fers the properties usually associated with a ferritic
5 stainless steel. It is a feature of the present inven-
tion that up to about 2% chromium is replaced by the
purposeful silicon addition without loss of oxidation,
especially cyclic, resistance.

Molybdenum additions are permitted up to about 5% to
10 promote a ferritic structure at all temperatures. It
also improves corrosion resistance and high temperature
creep strength.

Silicon is essential within the broad range of 0.8%
to about 2.25%, with a preferred range of about 1.0% to
15 about 2.0%. This silicon addition at least partially
replaces aluminum or higher chromium levels used in prior
art ferritic steels to provide high temperature (above
1500°F) oxidation resistance, and the replacement of
aluminum by silicon minimizes the detrimental effect of
20 aluminum on weldability. Silicon is of course a ferrite
former.

Aluminum is restricted to a broad maximum of about
2%, and for improved weldability is preferably restricted
to less than 0.5%. With titanium present, the nitrogen
25 in the steel preferentially combines with titanium rather
than aluminum, thereby avoiding the adverse effect of
aluminum nitrides in causing porosity in weld areas.

A carbide and nitride forming element is added in an
amount at least equal to the stoichiometric equivalent of
30 the carbon plus nitrogen contents. Titanium is preferred
and, if used, is present in a minimum amount of 4 times
the percent carbon plus 3.5 times the percent nitrogen.
A broad maximum of 1.0% should be observed, and a pre-
ferred maximum of 0.5% should be observed with carbon and
35 nitrogen each at a preferred maximum of 0.03%. When

1 titanium, aluminum and columbium are present, titanium
preferentially combines with nitrogen, and probably with
carbon, although it is possible that some of the carbon
may combine with columbium. The objective is to tie up
5 as much as possible of the carbon and nitrogen with
titanium or other carbide and nitride formers, leaving
columbium present in uncombined form.

Uncombined columbium is preferably used when
chromium plus molybdenum is at least 8% and is limited to
10 a broad maximum of 0.5%, and preferably to a maximum of
0.3%. At least 0.1% free or uncombined columbium is the
minimum effective amount. For reasons explained above,
the titanium addition permits the amount of total
columbium addition to be minimized, which is advantageous
15 from the standpoint of cost. The amount of uncombined
columbium needed for increased creep strength at elevated
temperature has been found to be relatively low, and as
little as 0.10% and preferably about 0.20% uncombined
columbium has been found to be effective for these
20 purposes, due to the synergistic effect of the silicon
addition.

Nickel may be added in amounts up to about 5% where
additional toughness is needed, if the level of ferrite
formers is high enough to avoid excessive austenite
25 formation, i.e., less than 10% austenite, and preferably
less than 5%.

Any one or more of the preferred ranges indicated
above can be used with any one or more of the broad
ranges for the remaining elements set forth above.

30 A series of experimental heats of steels of the
invention has been prepared and tested, along with
comparative steels in which silicon or columbium are
outside the ranges of the present invention. Comparative
tests have also been run on Type 409 and on the steel of
35 United States Patent 4,261,739. The compositions of

1 these steels are set forth in Table I.

Creep strength, as measured by sag resistance tests, is reported in Table II for 0.060 inch sheet at 1600°F, and in Table III for 0.045 inch sheet at 1500°F. It will be noted that several different final anneal temperatures were used, and the results show that a high temperature final anneal at 1850° to 2050°F significantly improves the sag resistance and hence creep strength of the cold rolled sheet. Heats 6 and 7 in Table II exhibited improved creep strength after anneals at 1950°F and 2050°F, respectively, in comparison to an anneal at 1850°F. In contrast to this, Heat 8, containing 0.44% silicon but otherwise within the composition limits of the steel of the invention, exhibited inferior sag resistance after an anneal at 1950°F, in comparison to an anneal at 1850°F. A representative steel of U.S. Patent 4,261,739, was inferior to Heat 7 after a final anneal at 1950°F.

Referring to Table III, Heats 9 and 10, which contained 1.94% and 2.42% silicon respectively, but no columbium, were inferior to Heats 4 and 5 (containing columbium) in sag resistance at the annealing temperature of 1950°F.

Referring to the drawing it is noted that a series of non columbium bearing steels exhibited a substantial increase in sag resistance as silicon was gradually increased, when the steels were subjected to a final anneal at 1950°F. On the other hand when the same steels were subjected to a final anneal at 1650°, the sag resistance decreased with increasing silicon contents. In both cases the effect is substantially linear.

Table IV summarizes mechanical properties of Heats 4 and 5 under different final annealing conditions. It will be noted that the yield strength and tensile strength of samples subjected to annealing at 1950°F are

1 slightly lower than those annealed at 1650°F but the
elongation values are somewhat higher.

5 Table V summarizes Olson cup values of Gas Tungsten
Arc autogenous weldments of a steel of the invention and
three comparative steels. It will be noted that the
formability and ductility of the weld areas in the steel
of the invention were relatively high. Heat 10,
containing 2.42% silicon, exhibited low values, thus
establishing criticality of the maximum of 2.25% silicon.
10 Heat 11, a steel of U.S.P. 4,261,739, was inferior to the
steels of the invention in weldability due to its
aluminum content of 0.91%.

Table VI contains cyclic oxidation resistance test
results conducted at 1700°F while Table VII contains
15 similar test results conducted at 1750°F. The use of
cyclic oxidation resistance tests rather than static
tests is believed to simulate more closely the particular
application of the steel of the present invention for
engine exhaust components. Accordingly, improved cyclic
20 oxidation resistance is of greater significance than
static oxidation resistance. It is evident from Tables
VI and VII that Heats 4 and 5, these being steels of the
invention, have cyclic oxidation resistance substantially
superior to that of Heat 12 which is the conventional
25 Type 409 alloy currently used for engine exhaust
components. On the other hand, Heat 11 which is a steel
of United States Patent 4,261,739, is definitely superior
to all the steels which were tested.

From the above description it is evident that the
30 invention includes within its scope alloy steel strip,
sheet, plate, bar, rod and wire annealed at 1850° to
2050°F having the above broad composition which exhibits
improved cyclic oxidation resistance and creep strength
at temperatures above 1000°F. Good results are obtained
35 at temperatures of at least 1500°F and up to about 1600°F

1 or higher in the higher chromium alloys, i.e. where
chromium is from about 6% to 25%, chromium plus
molybdenum total at least 8%, and at least 0.1%
uncombined columbium is present.

5 In one embodiment of the steel of the invention
chromium ranges from about 1% to about 8%, and no
uncombined columbium is present. In another embodiment,
which is ferritic at all temperatures, chromium ranges
from about 6% to about 25%, with the sum of chromium plus
10 molybdenum being at least 8%, and at least 0.1%
uncombined columbium is present.

An embodiment exhibiting an optimum combination of
properties consists essentially of 0.03% maximum carbon,
about 1% maximum manganese, about 1.4% silicon, about 11%
15 chromium, 0.03% maximum nitrogen, about 0.5% maximum
titanium with a minimum titanium content of 4 times the
percent carbon plus 3.5 times the percent nitrogen, about
0.2% uncombined columbium, less than 0.5% aluminum, and
balance essentially iron.

20 The invention further provides a welded article for
high temperature service fabricated from alloy steel
strip, sheet, plate, bar, rod and wire, which has been
subjected to a final anneal at 1850° to 2050°F and
exhibiting improved formability, cyclic oxidation
25 resistance and creep strength at temperatures above
1000°F, the steel having the broad composition set forth
above. Improved cyclic oxidation resistance and creep
strength at temperatures of at least 1500°F are obtained
in the ferritic steel alloy where chromium ranges from
30 about 6% to 25%, chromium plus molybdenum total at least
8%, and at least 0.1% uncombined columbium is present.

Automotive exhaust components for high temperature
service are provided by the invention fabricated from
alloy steel having the broad composition set forth above
35 and exhibiting improved cyclic oxidation resistance and

1 creep strength at temperatures above 1000°F. Improved
cyclic oxidation resistance and creep strength at
temperatures of at least 1500°F are obtained in ferritic
automotive exhaust components of the invention where
5 chromium ranges from about 6% to 25%, chromium plus
molybdenum total at least 8%, and at least 0.1%
uncombined columbium is present.

The invention also provides forged, cast and powder
metal articles having the broad composition set forth
10 above. Improved cyclic oxidation resistance and creep
strength at temperatures of at least 1500°F are obtained
in ferritic articles of the above type where chromium
ranges from about 6% to 25%, chromium plus molybdenum
total at least 8%, and at least 0.1% uncombined columbium
15 is present.

The steel of the present invention achieves the
objective of providing improved cyclic oxidation
resistance and creep strength at elevated temperature, in
comparison to the conventional Type 409, together with
20 improved weldability and creep strength as compared to
the steel of United States Patent 4,261,739 with a
reduction in expensive columbium as allowed by the
discovery of the unique synergistic effect introduced by
silicon when present in the alloys of this invention.

25

30

35

TABLE I

Compositions - Weight Percent

Heat No.	C	Mn	P	S	Si	Cr	Ni	Al	Ti	N	Cb
1	.023	.27	.023	.016	1.18	6.49	.19	.026	.35	.014	-
2	.022	.28	.021	.016	1.18	8.21	.19	.027	.35	.012	-
3	.025	.26	.022	.016	1.13	9.88	.18	< .020	.21	.012	-
4*	.019	.28	.023	.010	1.09	10.27	.18	.028	.31	.016	.15
5*	.020	.28	.022	.010	1.10	10.19	.19	.030	.33	.018	.29
6*	.020	.40	.020	.005	1.03	11.27	.43	.024	.22	.015	.19
7*	.019	.40	.020	.005	1.53	11.27	.43	< .020	.18	.015	.19
8	.019	.40	.020	.005	.44	11.27	.43	.024	.24	.015	.19
9	.015	.27	.021	.011	1.94	11.04	.20	.052	.41	.016	-
10	.018	.27	.021	.010	2.42	11.06	.20	.049	.43	.014	-
11**	.030	.33	.016	.011	.70	11.66	.22	.91	.44	.016	.52
12***	.014	.28	.019	.002	.58	11.15	.17	.060	.41	.012	-
13	.015	.26	.022	.011	1.45	11.08	.20	.047	.35	.015	-

*Steels of the invention

**Steel of U.S.P. 4,261,739

***Type 409

TABLE IISag Resistance - 1600°F 0.060" Sheet

<u>Heat No.</u>	<u>%Si</u>	<u>Sag Deflection - Inch</u>	
		<u>20 hrs.</u>	<u>100 hrs.</u>

1850°F Final Anneal

6*	1.03	0.065	0.160
7*	1.53	0.058	0.135
8	0.44	0.283	0.887

1950°F Final Anneal

6*	1.03	0.048	0.112
7*	1.53	0.029	0.069
8	0.44	0.591	> 1.350
Steel of USP 4,261,739		0.05	0.10

2050°F Final Anneal

6*	1.03	0.027	0.061
7*	1.53	0.028	0.058
8	0.44	0.258	0.742

* Steels of the invention

TABLE IIISag Resistance - 1500°F

<u>Heat No.</u>	<u>% Si</u>	<u>Sag Deflection - Inch</u>	
		<u>20 hrs.</u>	<u>100 hrs.</u>

1650°F Final Anneal

3*	1.13	.136	.262
9*	1.94	.225	.474
10	2.42	.328	.561
13*	1.45	.193	.420

1950°F Final Anneal

4**	1.09	.031	.052
5**	1.10	.045	.067
9	1.94	.072	.128
10	2.42	.051	.107
13	1.45	.083	.143

Average of duplicate samples - samples .045"
sheet except 9 and 10 which were 0.040" sheet.

* annealing treatment outside of invention

** Steels of the invention

TABLE IVMechanical Properties

Heat No.	Final Anneal °F	0.2% Y.S. ksi	U.T.S. ksi	% Elong. in 2"	Hardness HR _B
4	1650	39.7	67.2	32.5	75.5
4*	1950	36.1	61.6	34.5	74
5	1650	48.6	75.6	24	81.5
5*	1950	37.3	82.3	25.5	79.5

* Steels of the invention

TABLE VOlsen Values - Welds

<u>Heat No.</u>	<u>Orientation</u>	<u>Cup Height - In.</u>
3	Root	.368
	Face	.358
5*	Root	.335
	Face	.353
10	Root	.215
	Face	.318
11	Root	.203
	Face	.181

* Steels of the invention

TABLE VI

Cyclic Oxidation Resistance - 1700°F
Weight Gain in mg/cm²

<u>Heat No.</u>	<u>Cycles</u>				
	<u>142</u>	<u>274</u>	<u>373</u>	<u>613</u>	<u>948</u>
1	6.89	10.51	12.54	20.94	41.59
2	.45	.69	.82	.98	1.18
3	.26	.35	.38	.44	.50
5*	.38	.52	.65	.73	.85
9	.42	.60	.76	.88	1.01
10	.46	.66	.70	.96	1.06
11	.16	.15	.17	.19	.23
12	.83	-	1.21	2.22(after 752 cycles)	

Average of duplicate samples

* Steels of the invention

TABLE VIICyclic Oxidation Resistance - 1750°FWeight Gain in mg/cm²

<u>Heat No.</u>	<u>Cycles</u>	
	<u>59</u>	<u>240</u>
1	30.70	80.33
2	3.05	8.06
3	3.02	4.10
4*	.34	.69
5*	.38	.69
9	.39	.70
10	.38	.70
11	.30	.31
12	8.59	28.50

Average of duplicate samples
except Ht. 11

* Steels of the invention

1 **Claims:**

1. Annealed ferritic steel exhibiting improved
cyclic oxidation resistance and creep strength at
temperatures of at least 1500°F (816°C), after a final
5 anneal at 1850° to 2050°F (1010 to 1120°C), consisting
essentially of, in weight percent, 0.05% maximum carbon,
about 2% maximum manganese, 1.0% to 2.0% silicon, 6% to
25% chromium, up to about 5% molybdenum, with the sum of
chromium and molybdenum being at least 8%, 0.05% maximum
10 nitrogen, at least one of titanium, zirconium, tantalum
and columbium, with said titanium, zirconium, tantalum
and columbium being present in an amount at least equal
to the stoichiometric equivalent of the percent carbon
plus the percent nitrogen, and containing at least 0.1%
15 uncombined columbium, less than 0.5% aluminum, and
balance essentially iron.

2. The steel claimed in claim 1, consisting
essentially of about 0.03% maximum carbon, about 1%
maximum manganese, about 1.0% to about 2.0% silicon,
20 about 8% to about 20% chromium, about 0.5% maximum
molybdenum, about 0.03% maximum nitrogen, about 0.5%
maximum titanium with a minimum titanium content of 4
times the percent carbon plus 3.5 times the percent
nitrogen, about 0.3% maximum columbium with at least
25 0.10% uncombined columbium, less than 0.5% aluminum, and
balance essentially iron.

3. The steel claimed in claim 1 or 2, including up
to about 5% nickel.

4. The steel claimed in claim 1 or 2, wherein said
30 uncombined columbium is at least about 0.2%.

5. A ferritic steel as claimed in claim 1,
exhibiting good formability and improved cyclic oxidation
resistance and creep strength at temperatures of at least
1500°F (816°C) after a final anneal at 1850° to 2050°F
35 (1010° to 1120°C), consisting essentially of, in weight

1 percent, 0.03% maximum carbon, about 1% maximum
manganese, about 1.4% silicon, about 11% chromium, 0.03%
maximum nitrogen, about 0.5% maximum titanium with a
minimum titanium content of 4 times the percent carbon
5 plus 3.5 times the percent nitrogen, about 0.2%
uncombined columbium, less than 0.5% aluminum, and
balance essentially iron.

6. Alloy steel strip, sheet, plate, bar, rod and
wire annealed at 1850° to 2050°F which exhibits improved
10 oxidation resistance and creep strength at elevated
temperatures of at least 1500 (816°C), said steel
consisting essentially of, in weight percent, 0.05%
maximum carbon, about 2% maximum manganese, 1.0% to 2.0%
silicon, 6% to 25% chromium, up to about 5% molybdenum,
15 with the sum of chromium and molybdenum being at least
8%, 0.05% maximum nitrogen, at least one of titanium,
zirconium, tantalum and columbium, with said titanium,
zirconium, tantalum and columbium being present in an
amount at least equal to the stoichiometric equivalent of
20 the percent carbon plus the percent nitrogen, and
containing at least 0.1% uncombined columbium, less than
0.5% aluminum, and balance essentially iron.

7. Welded article for high temperature service
fabricated from alloy steel strip, sheet, plate, bar, rod
25 and wire which has been subjected to a final anneal at
1850° to 2050°F (1010° to 1120°C) and exhibiting improved
formability, cyclic oxidation resistance and creep
strength at temperatures of at least 1500°F (816°C), said
steel consisting essentially of, in weight percent, 0.05%
30 maximum carbon, about 2% maximum manganese, 1.0% to 2.0%
silicon, 6% to 25% chromium, up to about 5% maximum
molybdenum, with the sum of chromium and molybdenum being
at least 8%, about 0.05% maximum nitrogen, a carbide and
nitride forming element chosen from the group consisting
35 of titanium, zirconium, tantalum, columbium, and mixtures

1 thereof, said element being present in an amount at least
equal to the stoichiometric equivalent of the percent
carbon plus the percent nitrogen, and containing at least
0.1% uncombined columbium, less than 0.5% aluminum, and
5 balance essentially iron.

8. Automotive exhaust components for high
temperature service fabricated from an alloy steel which
has been subjected to a final anneal at 1850° to 2050°F
(1010° to 1120°C) and exhibiting improved cyclic
10 oxidation resistance and creep strength at temperatures
of at least 1500°F (816°C) said steel consisting
essentially of in weight percent, about 0.05% maximum
carbon, about 2% maximum manganese, 1.0% to 2.0% silicon,
6% to 25% chromium, up to about 5% maximum molybdenum,
15 with the sum of chromium and molybdenum being at least
8.0% about 0.05% maximum nitrogen, a carbide and nitride
forming element chosen from the group consisting of
titanium, zirconium, tantalum, columbium and mixtures
thereof, said element being present in an amount at least
20 equal to the stoichiometric equivalent of the percent
carbon plus the percent nitrogen, and containing at least
0.1% uncombined columbium, less than 0.5% aluminum, and
balance essentially iron.

9. Forged, cast and powder metal articles
25 consisting essentially of in weight percent, about 0.05%
maximum carbon, about 2% maximum manganese, 1.0% to 2.0%
silicon, 6% to 25% chromium, up to about 5% maximum
molybdenum, with the sum of chromium and molybdenum being
at least 8.0%, about 0.05% maximum nitrogen, a carbide
30 and nitride forming element chosen from the group
consisting of titanium, zirconium, tantalum, columbium,
and mixtures thereof, said element being present in an
amount at least equal to the stoichiometric equivalent of
the percent carbon plus the percent nitrogen, and
35 containing at least 0.1% uncombined columbium, less than
0.5% aluminum, and balance essentially iron.

0145471

1 / 1

